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ON THE SOLID STATE REACTIONS IN THE SYSTEM Mn—Si—N

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ABSTRACT

The reaction processes involving the formation and decomposition of manganese silicon nitride $MnSiN_2$ have been investigated. Thermochemical analysis in nitriding, inert and oxidizing atmospheres was carried out for this nitride and the appearing intermediate phases The investigation was performed using TG, DTA and DTG techniques in the temperature range 25—1500°C.

INTRODUCTION

Previous investigations conducted in the system Mn—Si—N have involved treatment of the mixtures of Mn(s) and silicon nitride (Si_3N_4) or manganese silicate ($MnSiO_3$) with ammonia [1] and also treatment of the mixtures of Mn(s) and manganese silicide (MnSi) and Si(s) with N_2(g) [2] at constant temperatures up to 1250°C. The product obtained is an orthorombic manganese silicon nitride of formula $MnSiN_2$.

This compound has also been detected as a second-phase precipitate in heat-treated Mn, Si-steels [3—5]. Moreover, it has been found possible to precipitate $MnSiN_2$ by nitriding Fe—Mn—Si alloys with various NH_3/H_2 mixtures at 400—800°C [6—9]. The solubility of $MnSiN_2$ in ferrite and the related thermodynamic properties have been investigated [10]. Below 670°C triclinic and hexagonal $MnSiN_2$ forms are obtained, while above 700°C the orthorombic form is always obtained. The nitriding temperature and also the Mn · Si ratio and the oxygen potential in the alloy are suggested to be the factors determining the structural form of the nitride.

The oxidation properties of $MnSiN_2$ have been studied and the oxidation product at 1000°C was found to be $MnO \cdot 3\,Mn_2O_3 \cdot SiO_2$ (braunite) and amorphous SiO_2 [1,9].

The aim of the present work was to investigate the reaction processes and the products which appear during the formation of $MnSiN_2$ when various Si : Mn powder mixtures are treated in N_2(g) (P_{N_2} = 1 atm). Another aim was to study some of the thermochemical properties and the behaviour of the products which are formed in oxidizing and inert atmospheres. The techniques of TG—DTG—DTA together with X-ray diffractometry (XRD) at room temperature and IR spectroscopy were employed. $MnSiN_2$ is suggested [2] as a possible component of new materials (M_x(Si, Al)N_2). As a second-phase precipitate it is responsible for the inhibition of strain aging in low-carbon steels.

EXPERIMENTAL

The TG—DTG—DTA measurements were made using a microthermobalance (Mettler TAI). Mixtures of Mn (99.9%) and Si (99.9%) powders (1—20 μ) in molar ratios 1 : 2, 1 : 1 and 2 : 1 were treated in N_2(g) and Ar(g) in the range 25—1500°C.

The intermediary and final products obtained during the reaction processes were identified by XRD and IR spectroscopy. Auxiliary runs were then made where these products were reacted in such a way as to identify the various stages of $MnSiN_2$ formation.

The reactions between Mn powder and silicon nitride (<95% of the β-form) and the decomposition and oxidation of $MnSiN_2$ were also studied up to 1200°C. The experimental conditions and parameters were predominantly similar to those described previously [9,11].

RESULTS AND DISCUSSION

1 *Formation of $MnSiN_2$*

1.1 *Mn, Si powder mixtures in N_2(g)*

The reaction processes which occur when a mixture of 1 mole Si and 1 mole Mn powder is treated in N_2(g) up to 1480°C (10°C min^{-1}) are illus-

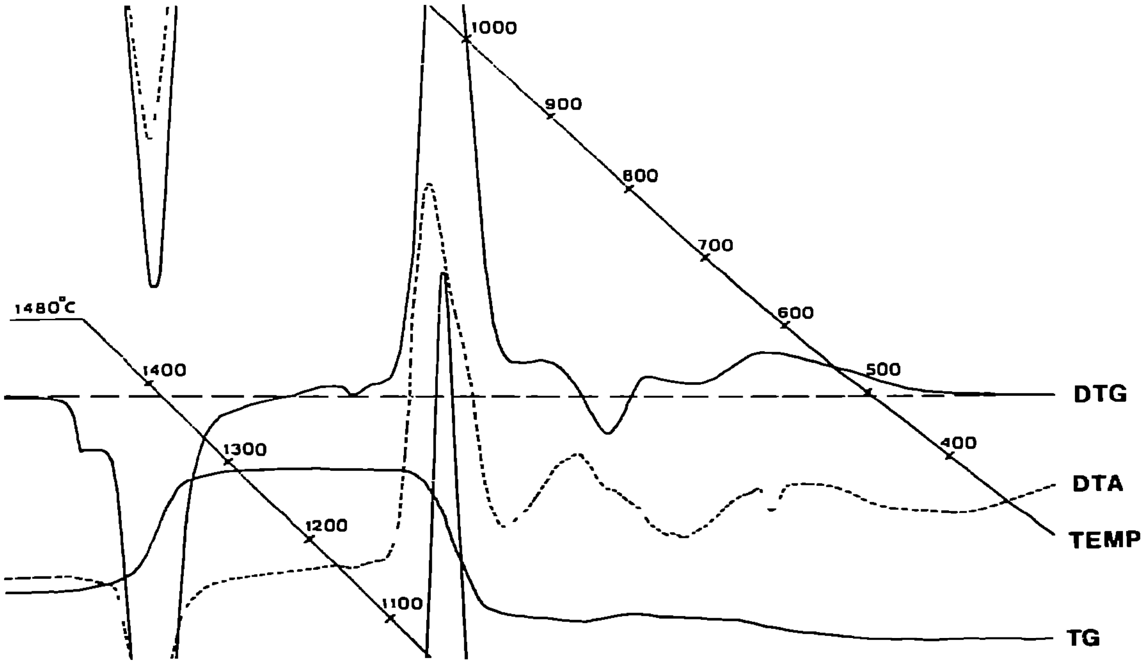

Fig. 1. Nitridation of the mixture Mn : Si = 1 : 1 in N_2(g) at 10°C min^{-1}.

trated by the typical thermogram in Fig. 1. The DTA curve suggests three reaction steps (peaks) initiated at approximately 470, 700 and 950°C. They are followed by a decomposition at approximately 1300°C.

The first peak is due to the reaction of Mn with $N_2(g)$ to form the ϵ-phase ($\approx Mn_4N$) [17]. This phase is thus the starting product for the reaction with Si which occurs during the second reaction step (700—950°C). XRD analysis of specimens obtained after this step (cooled from 950°C) showed the presence of MnSi and a certain amount of $MnSiN_2$. After the completion of the third step the TG and XRD data indicated the presence of a single phase: the orthorombic $MnSiN_2$ This phase starts to decompose at an appreciable rate at about 1300°C.

The products after cooling from 1480°C consists of a grey powder identified as Si_3N_4 (predominantly α) and droplets of solidified melt containing the silicides Mn_3Si and Mn_5Si_3 [12,13]. In the Mn—Si phase diagram [12] the pure melt phase is shown to appear at ~1275°C for MnSi. The beginning of rapid decomposition of $MnSiN_2$ was observed at approximately 1300°C Thus $MnSiN_2$ seems to become unstable in the Mn, Si-melt and decomposes to silicon nitride at 1 atm N_2 pressure.

Figure 2 illustrates the reactions of the Mn/Si powder mixtures in the molar ratio 1 : 2 (Si surplus) up to 1400°C (10°C min^{-1}) in $N_2(g)$ It can be seen that the initial two DTA exothermal reactions (the first at ~470°C and the second at ~730°C) are similar to those in Fig. 1. The products obtained after cooling from 1000°C consisted mainly of $MnSi_{1.73}$ [13,14] with some MnSi, unreacted Si traces of $MnSiN_2$.

After these exothermal processes the reaction between the Si-rich silicide $MnSi_{1.73}$ and $N_2(g)$ appears to be sluggish as compared to that in Fig. 1. The large endothermal DTA peak at 1122°C indicates melting of $MnSi_{1.73}$. This

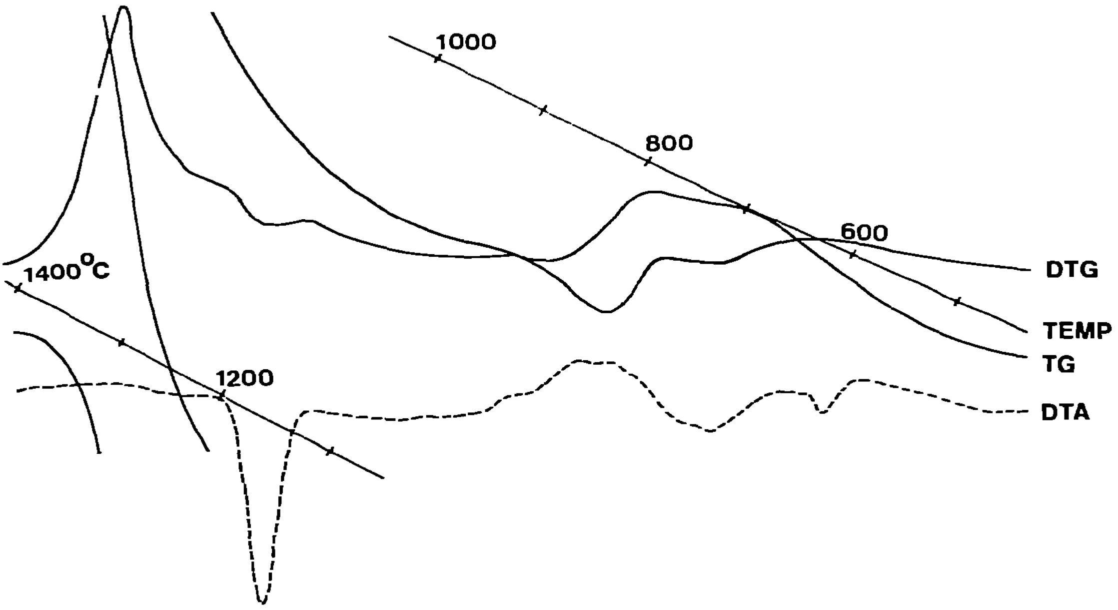

Fig. 2. Nitridation of the mixture Mn . Si = 1 : 2 in $N_2(g)$ at 10°C min^{-1}.

temperature is in good agreement with the lower experimental points given for the eutectic line for the partial system MnSi—Si [12,16].

The reaction with the melt is then seen to proceed without any observable change of enthalpy (DTA). The products obtained at approximately 1400°C have been identified as α- and some β-Si_3N_4 together with the silicides Mn_5Si_3 and MnSi. On heating the mixture Mn : Si = 1 : 2 in N_2(g) up to a maximum of 1200°C, $MnSiN_2$ was obtained (together with almost pure α-Si_3N_4).

The processes involving the mixtures Mn : Si = 2 : 1 (Mn surplus) followed a similar path to that already described up to approximately 950°C. After the second exothermal step (950°C) the products are Mn_3Si, Mn_5Si_3 and some $MnSiN_2$. These Mn-rich silicides then react with nitrogen about as rapidly as does MnSi (see also sect. 4). According to the phase diagram [12] Mn_3Si decomposes peritectically already at 1075°C. The rate of N uptake ($MnSiN_2$ formation) does not seem to be affected immediately above this temperature. A marked DTA endothermal peak appears at 1170°C, indicating that the remaining unreacted silicides approached into the melt phase region. The specimen then began to rapidly give off nitrogen, again indicating the instability of $MnSiN_2$ against the Mn—Si melt. The products below 1150°C consisted of $MnSiN_2$ and a mixture of Mn nitride phases (ε and ζ) [12,17,18].

1.2 Mn, Si powder mixtures in Ar(g)

DTA runs were made with the mixtures of Mn, Si powders (in molar ratios as above) in argon at 10°C min^{-1} up to 900°C. All three mixtures showed the same kind of exothermal reaction (DTA peak) in the range 700—850°C. This peak is shown in the first part of Fig. 5.

In the phase diagram Mn—Si, the lowest temperature at which the appearance of a liquid phase is expected is 1040°C. This suggests that the reaction between Mn and Si proceeds by a solid-state mechanism. Its rate seems to be too high for it to be controlled by the presence of low-melting point eutectica formed by the impurities (~0.1 w/o) present in Mn and Si.

The silicide products obtained after cooling from 900°C were the same as those identified after the second reaction step (750—950°C, Fig. 1) in N_2(g). Excepting the mixture Mn : Si = 1 : 2, these are consistent with those expected according to the Mn—Si phase diagram. A certain amount of MnSi and Si was also found in this case. The structure of $MnSi_{1.73}$ is complex and its unit cell content is consistent with the formula $Mn_{15}Si_{27}$ [14] ($Mn_{27}Si_{47}$ when displaying superstructure) [15]. The mechanism of formation of this compound may therefore be expected to be more intricate than that for MnSi which may then appear as a side-product for merely kinetical reasons.

1.3 Reactions of Mn_4N with Si and silicates in Ar(g)

As indicated in Fig. 1 the DTG curve decreased below the zero level during the second exothermal reaction step (750—950°C), indicating nitrogen loss by the specimen. As already shown in sect. 1.1, the main process here is the reaction of ε-Mn nitride (≈Mn_4N) with Si to form silicides. However, variable amounts of $MnSiN_2$ were also obtained.

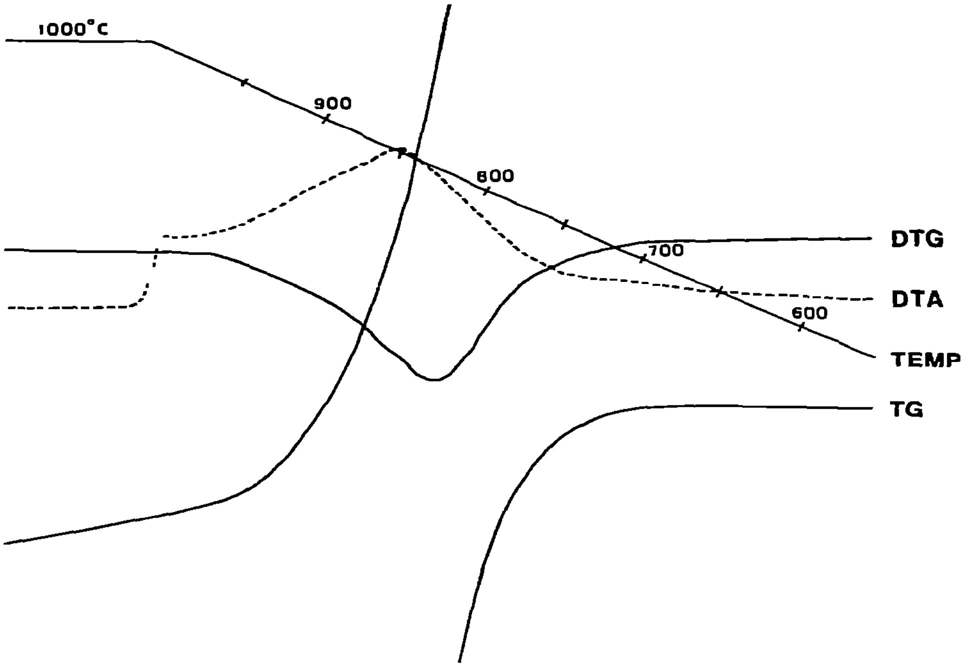

Fig 3. Reaction of the mixture Mn_4N . Si = 1 · 1 in Ar(g) at 10°C min^{-1}.

In order to investigate the nature of this reaction step, mixtures of Si and separately prepared ε-nitride with the stoichiometric composition Mn_4N (in the same Mn : Si ratios as before) were reacted in an Ar atmosphere.

As shown in Fig. 3, for the mixture of 1 mole Mn_4N and 2 moles Si (Mn Si = 2 : 1), the initial stage of this reaction is similar to that in N_2(g) (Figs. 1 and 2). Also, the maximum rate of N_2 loss (DTG) was obtained at the same temperature as that in the nitrogen atmosphere. This indicates that the reaction process is dominated by the formation of silicide.

Figure 4 shows the N loss of Mn_4N/Si and Mn_4N/MnSi mixtures in comparison to the N loss of pure Mn_4N in an Ar atmosphere. In the presence of free Si the rate of N loss at 750—950°C is seen to be essentially higher than that of pure Mn_4N. Nevertheless, unlike the decomposition curve for Mn_4N the curves for Si-containing specimens are shown to stabilize after about 10 min at 1000°C. This indicates that a part of the nitrogen from Mn_4N was taken up by the specimens. The Mn-richer mixtures retained about 50% of N while only 30% was taken up by the mixture of Mn_4N—8 Si. This is also consistent with the observed sluggish reaction of this Si-rich mixture in N_2(g) (Fig. 2).

The products of these reactions are Mn silicides and $MnSiN_2$ which suggests that the $MnSiN_2$ formation also occurs via the Mn_4N phase. Three reaction paths may then be considered:

(a) direct reaction between Mn_4N and the silicides formed;

(b) reaction of silicides and N_2 gas released during Mn_4N decomposition; or

(c) direct formation of $MnSiN_2$ from Mn_4N and Si.

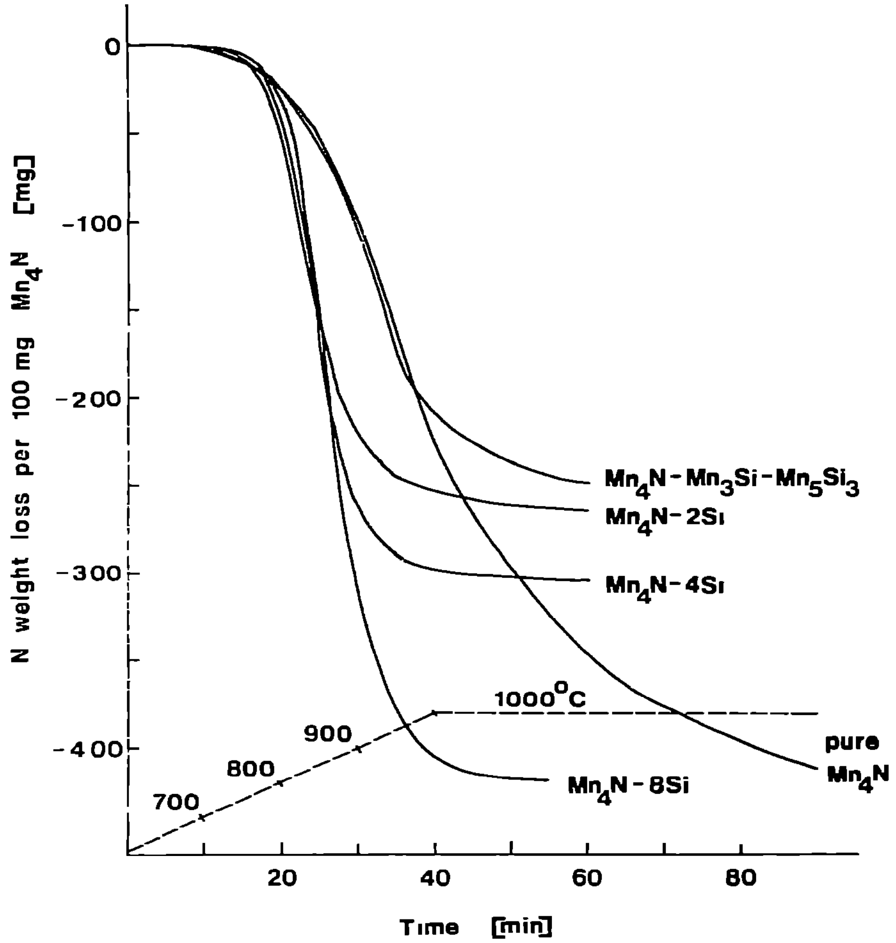

Fig. 4. Nitrogen weight loss per 100 mg Mn_4N (in mg) in Ar(g) at 1 atm for various mixtures Mn_4N—Si and Mn_4N—Mn_5Si_3, Mn_3Si compared to that of pure Mn_4N.

Path (a) was investigated by reacting a mixture of pure Mn_4N, Mn_5Si_3 and Mn_3Si in the molar ratio 1 : 1 : 1. The curve showing the N loss of this mixture is also given in Fig. 4. This curve is seen to follow the decomposition curve for pure Mn_4N until about 975°C. These silicides are thus shown to be inert towards Mn_4N below this temperature.

1.4 Reactions of silicides with $N_2(g)$

Reaction path (b) was studied as illustrated in Fig. 5 for the mixture Mn : Si = 1 . 1. At first, this mixture reacted in an argon atmosphere (DTA exothermal peak) to form MnSi. After completion of this reaction the atmosphere was changed to that of nitrogen gas. The silicide formed started to react with N to give $MnSiN_2$ at around 1000°C. The reaction process up to 1400°C was then the same as that shown in Fig. 1. In the runs with Mn_4N and Si in Ar (Figs. 3 and 4) the reaction leading to $MnSiN_2$ already reached completion at below 1000°C.

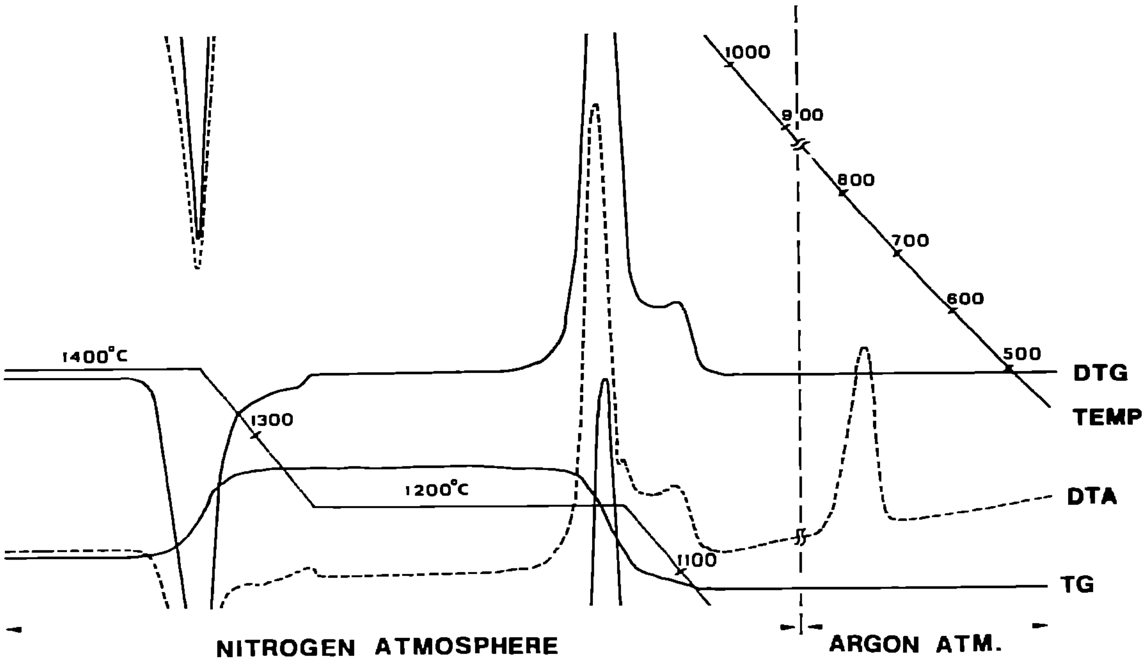

Fig 5. Reaction of the mixture of Mn Si = 1 : 1 in Ar(g) to give MnSi and nitridation of this silicide in N_2(g).

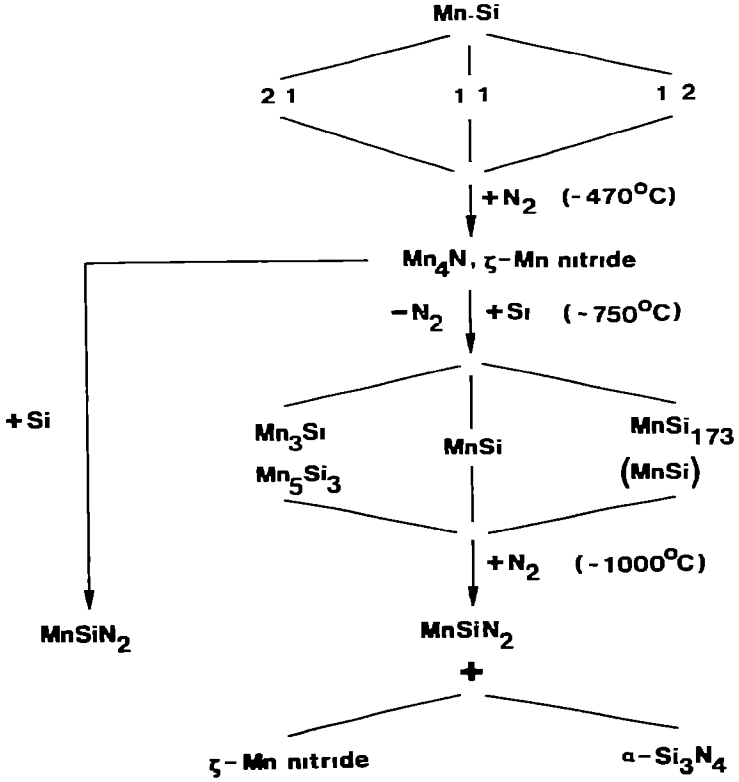

Fig. 6. Schematic outline of the process of formation of $MnSiN_2$ below 1150°C from the mixtures of Mn and Si powders in molar ratios 2 : 1, 1 : 1 and 1 : 2.

On the basis of these types of measurements a reaction scheme for the process of formation of $MnSiN_2$ has been arrived at (see Fig. 6). Here the mixtures of Mn and Si (at the molar ratios given) react with N_2 gas and, as a first step, Mn_4N (ϵ-nitride) is formed [16]. Above 882°C [18,19] this nitride decomposes to the ζ-nitride which is then the phase taking part in the further reactions. The next principal step involves the silicide formation accompanied by a loss of N. However, there is the previously identified parallel process [path (c)] where Si will react directly with the Mn nitrides to produce $MnSiN_2$. The silicides formed react with N to give $MnSiN_2$. As side-products, either ζ-nitride or α-Si_3N_4 are obtained below 1150°C when Mn or Si are present in excess. Of course, this scheme only provides a general outline of the reaction processes. More detailed investigations are needed to acquire a sufficient knowledge of the reaction mechanisms underlying these processes.

2. *Decomposition of $MnSiN_2$ in Ar(g)*

$MnSiN_2$ powder specimens were heated in Ar(g) up to 1030°C (10°C min^{-1}) in the thermobalance. Weight loss began at 750—770°C and the nitride started to decompose more rapidly at 830—840°C. As expected, the solid product of this decomposition was the silicide MnSi. After approximately 2 h at 960°C the N loss corresponded to about a 20% decomposition of $MnSiN_2$ to MnSi.

3 *Reaction of Si_3N_4 and Mn powders in Ar(g)*

It has already been demonstrated [1] that $MnSiN_2$ can form according to

$$3\ Mn + Si_3N_4 + 2\ NH_3 \rightarrow 3\ MnSiN_2 + 3\ H_2$$

In order to investigate whether there may be a solid-state reaction between only Mn and Si_3N_4, powder mixtures of Mn and Si_3N_4 (approximate $\beta : \alpha$ ratio 95 . 5) in molar ratios 3 : 1 and 1 . 1 were reacted in an argon atmosphere at temperatures up to 1200°C

For the mixture of Mn : Si_3N_4 = 3 . 1 the N loss was observed to start at 840°C. After holding the specimen at various constant temperatures between 950—1030°C for about 2.5 h the weight loss corresponded to 15% of the nitrogen bound as Si_3N_4. The X-ray diffraction pattern of the reacted specimen showed the presence of unreacted Mn and Si_3N_4 along with $MnSiN_2$ and the silicide Mn_3Si As has been shown earlier [11] Si_3N_4 is stable up to approximately 1200°C in Ar(g). The N loss observed is thus due to an interaction between Mn and Si_3N_4. The only compound which is expected to be formed is $MnSiN_2$. According to Sect. 3, $MnSiN_2$ decomposes at the same temperature as that observed for the present mixture. Thus, the presence of $MnSiN_2$ in the reaction products suggests that either this nitride formed in a sufficient amount at temperatures below 840°C or, that the rate of its formation from Mn and Si_3N_4 at temperatures above 840°C is higher than the rate of decomposition. As also shown above, MnSi is obtained as a decomposition product of $MnSiN_2$. This silicide then may react with the surplus Mn to give Mn_3Si. Thus, the probable parallel reactions can be summarized as follows

$$3\,Mn + Si_3N_4 \rightarrow 2\,MnSiN_2 + MnSi$$

$$MnSiN_2 \rightarrow MnSi + N_2$$

$$2\,Mn + MnSi \rightarrow Mn_3Si$$

Upon reacting the mixture Mn : Si_3N_4 = 1 : 1 the initiation of N loss was observed at 770°C (as for the decomposition of $MnSiN_2$). After approximately 2 h at 1200°C the weight of the specimen stabilized. The products of this reaction consisted of unreacted Si_3N_4 and Mn_5Si_3, no $MnSiN_2$ was detected. However, consideration of the previous results suggests that this nitride might appear as an intermediary phase which decomposes to MnSi. This silicide may then have taken part in a parallel reaction with Mn giving Mn_5Si_3.

These reactions are consistent with the observations made in Mn, Si-steels [5—7] which show that silicon nitride cannot be stable as a second-phase precipitate in the presence of manganese as long as the Mn activity is high enough to form $MnSiN_2$. The stability of this nitride then depends on the nitrogen activity at a given temperature. As shown in sect. 1.1, $MnSiN_2$ is not stable above 1200°C towards silicides. Si_3N_4 is stable above this temperature and is thus the phase appearing in N_2(g) at atmospheric pressure. In Ar(g) Si_3N_4 is attacked by Mn and the phase formed is a silicide such as Mn_5Si_3.

Silicon nitride is important as a refractory compound. The resistance of this nitride against manganese must be considered as very limited below 1200°C.

4. *Kinetics of the initial stage of $MnSiN_2$ formation*

As demonstrated qualitatively in the non-isothermal runs (Figs. 1 and 2) the rate of $MnSiN_2$ formation above 900°C is significantly lower for the mixture of Mn : Si = 1 : 2 than it is for Mn : Si $\geqslant$ 1 : 1. Isothermal runs were made in the initial stage of the reactions leading to $MnSiN_2$ in the range 800—950°C Within this limited range the amount of N taken up by the specimen was found to be a linear function of time at constant temperatures. This linear weight gain could be reproducibly observed up to a maximum 60% of the total N uptake corresponding to the stoichiometric amount required for the formation of $MnSiN_2$.

In order to compare the rates of nitride formation for the three different mixtures used, the N uptake is expressed as a weight gain (Δm in mg) of a mixture per 1 mmole of $MnSiN_2$ formed. The rate constant at constant temperature $k(T)$, is simply given as the change in weight gain per unit time (h), $k(T) = \delta\Delta m/\delta t$. The variation of $k(T)$ with temperature is assumed to obey an exponential relation of the Arrhenius-type which in logarithmic form reads

$$\log k(T) = \log A - \frac{B}{2.303\,RT}$$

A and B are usually interpreted as a frequency factor and an apparent activa-

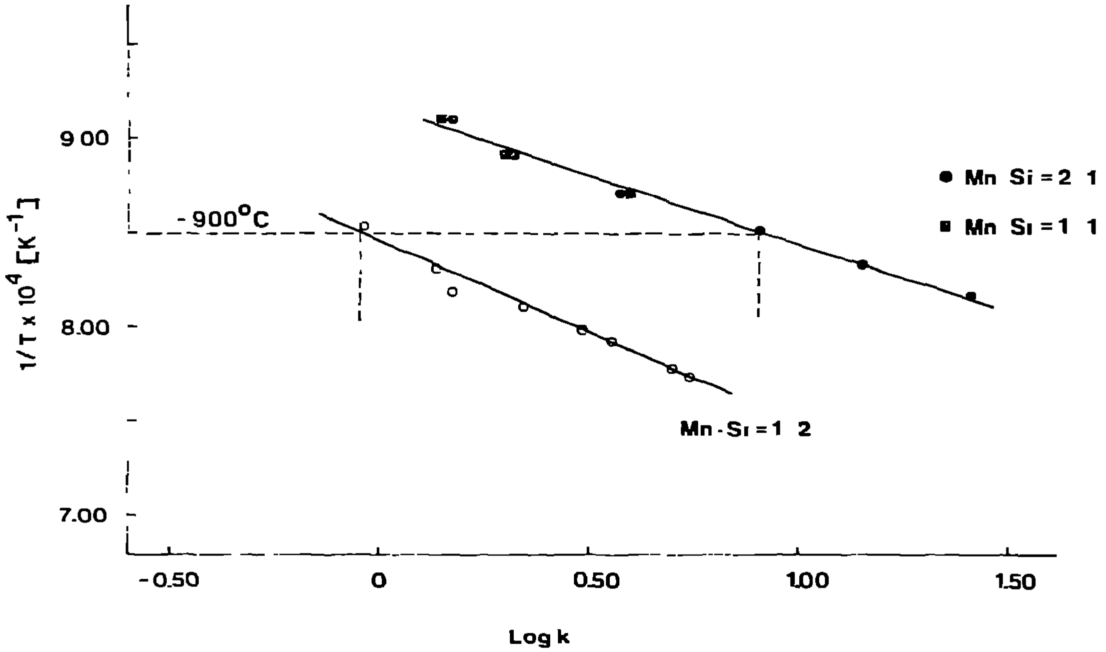

Fig. 7. The rate constant k as a function of reciprocal absolute temperature for the initial stage of $MnSiN_2$ formation from various Mn—Si mixtures, given as a weight gain (mg) per 1 mmole of $MnSiN_2$ formed per unit time (h).

tion energy, respectively. Figure 7 shows a plot of log k against the reciprocal temperature for the Mn : Si mixtures used. Within the temperature range studied the straight line realtionships appear to be valid. For the mixtures with Mn : Si $\geqslant$ 1 : 1 (forming the Mn-rich silicides Mn_3Si, Mn_5Si_3 and MnSi) the initial rates seem to be virtually identical. The mixture Mn : Si = 1 : 2 (forming predominantly $MnSi_{1.73}$) shows a significantly lower rate of nitride formation, in accordance with previous observations. At approximately 900°C (the dashed line in Fig. 7) the rate for this mixture is seen to be almost one order of magnitude lower than that for the Mn-richer mixtures. The slopes of the lines in Fig. 7 are not too different, indicating that the activation energies are of the same magnitude for both types of mixtures.

5. *Thermal analysis in oxidizing atmosphere*

Starting from the three Mn : Si mixtures used previously the phases (Sect. 1.1), consisting of essentially pure $MnSiN_2$ or $MnSiN_2$ and either α-Si_3N_4 (Si-surplus) or a mixture of ϵ- and ζ-nitrides (Mn-surplus), were prepared. The oxidation of pure $MnSiN_2$ was studied in air at temperatures up to 1000°C (10°C min^{-1}). This proceeded in a similar way to that observed previously [9] for $MnSiN_2$ powder which had been isolated from Mn—Si—N—Fe alloys. However, the pattern of the DTA responses was significantly different for the isolated [9] powders and those prepared synthetically from the pure Mn, Si powders in the present work. For the synthetic powder the weight gain was observed to start at approximately 350°C. A wide exothermal DTA peak was initiated at 500 ± 15°C. The oxidation rate attained a maximum (DTA, DTG) at about 680°C and decreased thereafter. A very sharp exothermal DTA peak, which was similar to that observed for the isolated powder at 895°C then appeared at 840—850°C. The decomposition of $MnSiN_2$ (sect. 3) was observed to start rapidly at temperatures close to 840°C. The oxidation products (braunite, silica) were suggested [9] to form a protective layer on the nitride grains. If the nitride beneath this layer decomposes above 840°C an increased N pressure will result and this pressure may cause this oxide layer crack. The nitride interface would then be exposed to the oxidizing atmosphere giving rise to the sharp exothermal DTA response observed. According to the earlier suggestion [9], the appearance of this response was correlated to the partial instability of the braunite oxidation layer rejecting some oxygen at approximately 880°C. However, since this response was already observed at 840°C in this investigation the mechanism proposed here seems to be the more likely one.

The typical particle size of the $MnSiN_2$ powder synthetically prepared in the present work was 1—10 μ compared to about 0.1 μ for the $MnSiN_2$ isolated from Fe-alloys. The particle size difference together with the formation of a protective layer are the factors which probably lead to different oxidation patterns for these two types of nitride specimens. This clearly illustrates the difficulty of applying the DTA data of synthetical nitrides to identifying the nitride residues isolated from steels. Nevertheless, in the present case $MnSiN_2$ can be identified according to the above-mentioned sharp DTA response appearing at 840—895°C.

Figure 8 shows an example of a more complex process where the mixture of $MnSiN_2$, ε- and ζ-Mn nitrides (prepared by nitriding the mixture of Mn ·

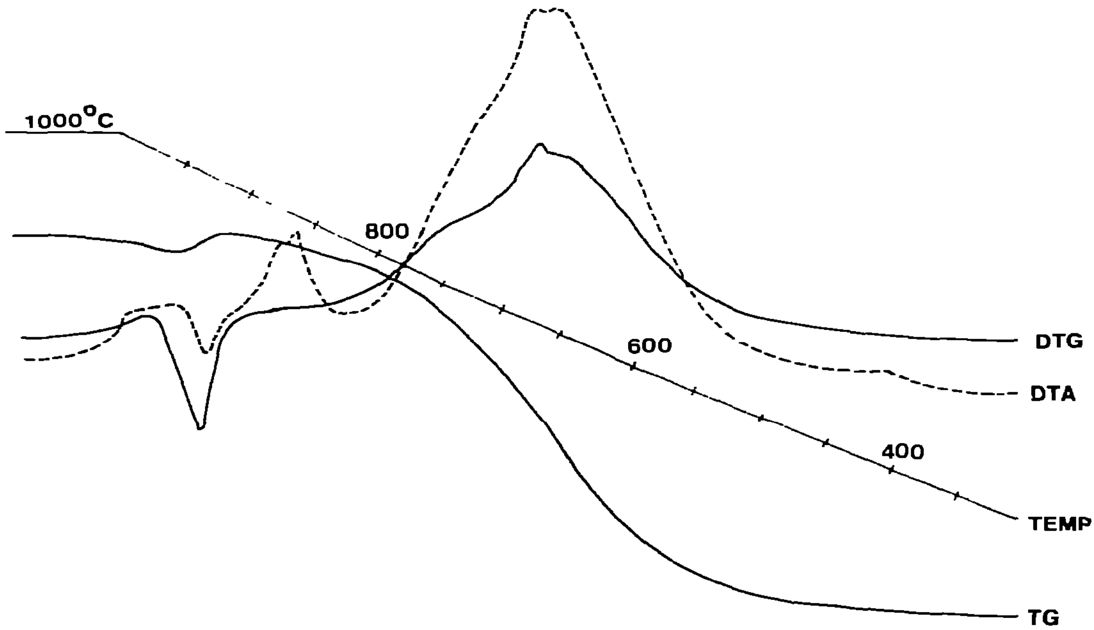

Fig. 8 Oxidation of a mixture of $MnSiN_2$ and ε- and ζ-Mn nitrides, which had been prepared by nitridation of the mixture of Mn : Si = 2 · 1, in air at 10°C min^{-1}.

Si = 2 : 1) was oxidized (10°C min^{-1}) in air. Of course, a phase mixture prepared in this way would be more compact than a mechanical mixture of separately prepared phases. Thus the pattern of the DTA and DTG responses is quite different from that expected [17] for these phases when mixed separately. However, $MnSiN_2$ still seems to be identifiable from the DTA exothermal response at approximately 840°C. The ensuing endothermal response at approximately 900°C is that of the decomposition of Mn_2O_3 (formed by oxidation of Mn nitrides) to Mn_3O_4. It gives an indirect indication of the presence of these nitrides.

On oxidizing the similarly prepared mixtures of α-Si_3N_4 and $MnSiN_2$, the oxidation process up to about 950°C was essentially equivalent to that for pure $MnSiN_2$. This nitride may thus be identified and determined selectively in the presence of silicon nitride. The calculation based on TG-data shows that this determination can be made with a maximum deviation of 6%, with respect to the amount of $MnSiN_2$ formed by nitridation of a Mn : Si mixture with molar ratio 1 : 2.

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